

# Correlation, relativistic, and adiabatic effects in the interaction of metastable helium atoms

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## The goal of the work

Accurate calculation of the **low-energy *s*-wave scattering length**  $a$  for the interaction of helium atoms in their lowest triplet state

## Motivation

- In 2001 the Bose-Einstein condensate (BEC) of spin-polarized  $\text{He}^*$  atoms was achieved:
  - this result offers new detection strategies exploiting the large internal energy (19.8 eV) of  $\text{He}^*$  atoms,
  - the analysis of BEC experiments using  $\text{He}^*$  depends strongly on the accuracy with which the scattering length is known.
- The uncertainty in  $a$  limits the understanding of the collective properties of the  $\text{He}^*$  gas in the hydrodynamic regime.
- Interpretation of simultaneous quantum degeneracy in dilute Bose-Fermi mixture of metastable  $^4\text{He}^*$  and  $^3\text{He}^*$  atoms.

# Scattering length – definition

- solve the radial Schrödinger equation for small energy  $E$

$$\psi''(E, R) + 2/R \psi'(E, R) + 2\mu/\hbar^2 [E - V(R)] \psi(E, R) = 0.$$

- find the phase shift  $\delta(k)$ , where  $k = \sqrt{2\mu E/\hbar^2}$ , by comparing the solution  $\psi$  with its proper asymptotic form

$$\psi(E, R) \sim \frac{1}{kR} (\sin kR + \tan \delta(k) \cos kR),$$

- behavior of the phase shift for small  $k$  gives the scattering length

$$a = - \lim_{k \rightarrow 0} \frac{\tan \delta(k)}{k}.$$

- the scattering length is finite provided the potential vanishes sufficiently fast with  $R$ :  $V(R) = O(R^{-l})$ , where  $l \geq 4$

# Scattering length – applications

The scattering length  $a$  fully characterizes interactions of cold atoms in the low-energy limit. Knowing  $a$  we can calculate:

- the scattering amplitude:  $f(\theta) = -a$ ,
- the differential cross section:  $\frac{d\sigma}{d\Omega} = a^2$ ,
- the total cross section:  $\sigma = 4\pi a^2$ ,
- the effective potential:  $V_{\text{eff}}(\mathbf{R}) = \frac{4\pi\hbar^2 a}{m} \delta(\mathbf{R})$ .

The sign of  $a$  determines the stability of the Bose-Einstein condensate with respect to the number of particles contained in it, and the magnitude of  $a$  determines the size of the condensate.

# Scattering length

The scattering length is very sensitive to the quality of the interatomic potential  $V(R)$ , so accurate theoretical prediction of  $a$  provides a serious challenge to *ab initio* calculations.

# The scattering length for spin-polarized helium. Situation in 2005.

Author (year)	$a$ [nm]
Experimental determinations	
Robert <i>et al.</i> (2001)	$20 \pm 10$
Pereira Dos Santos <i>et al.</i> (2001)	$16 \pm 8$
Tol <i>et al.</i> (2004)	$10 \pm 5$
Seidelin <i>et al.</i> (2004)	$11.3^{+2.5}_{-1.0}$
Theoretical determinations	
Gadéa <i>et al.</i> (2002), CCSD(T)	32.5
Gadéa <i>et al.</i> (2002), MRCI	15.4
Dickinson <i>et al.</i> (2004)	$12.2_{-4.2}$
Tol <i>et al.</i> (2004)	8.3

## Conclusions from previous theoretical attempts to determine a

- It is necessary to take into account all subtle electron correlation effects
- Very good long-range asymptotics of the interaction potential should be provided

## New ideas

- Adiabatic and relativistic corrections are only slightly smaller than the energy of higher electronic excitations and they also must be included
- Long-range asymptotics of these corrections should be provided
- Additional more subtle effects: QED correction and effect of retardation

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**Generation of a family of correlation consistent  
one-electron Gaussian basis sets especially suited  
for studies on the interaction of triplet helium atoms**

# Generation of Gaussian basis sets

1. 22  $s$  functions were fully optimized on the Hartree-Fock energy, and then contracted to give good description of the occupied  $1s$  and  $2s$  orbitals
2. polarization functions were optimized on the atomic correlation energy;  $XZ$  basis sets, with the cardinal number  $X = 3 - 7$ , have the composition  $(X + 2)s Xp (X - 1)d (X - 2)f \dots$
3. exponents of diffuse functions were optimized directly on the van der Waals coefficients  $C_6^{(2)} - C_{16}^{(2)}$ ; singly and doubly augmented basis sets  $aXZ$  and  $dXZ$ , respectively
4. in addition, two different sets of bond functions were used

**High accuracy calculations of the Born-Oppenheimer interaction energy, and adiabatic, relativistic and QED corrections for finite interatomic distances**

The interaction energies for finite interatomic distances were obtained as a sum of two contributions

$$V = V_{\text{CCSD(T)}}(A) + \delta V_{\text{FCI}}(B),$$

where

$$\delta V_{\text{FCI}}(B) = V_{\text{FCI}}(B) - V_{\text{CCSD(T)}}(B).$$

The FCI correction is only a small fraction of the CCSD(T) energy (usually about 0.5%), so the basis set B could be significantly smaller than A.

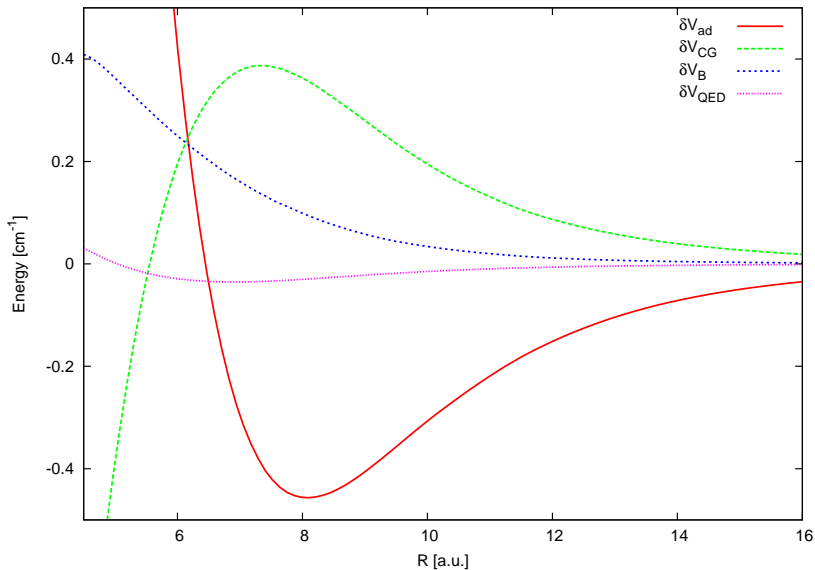
Both contributions were extrapolated independently to the complete basis set (CBS) limit using a simple two-point formula

$$V(X) = V(\infty) + AX^{-5}.$$

# Corrections to the interaction potential

- $\delta V_{\text{ad}}$  of order  $m/M$  – adiabatic correction, calculated using the Born-Huang formula as expectation value of  $T_n$
- $\delta V_{\text{CG}}$  of order  $\alpha^2$  – relativistic correction in the Cowan-Griffin approximation, sum of expectation values of  $H_{\text{MV}}$  and  $H_{\text{D1}}$
- $\delta V_{\text{B}}$  of order  $\alpha^2$  – Breit correction, expectation value of  $H_{\text{OO}}$
- $\delta V_{\text{QED}}$  of order  $\alpha^3$  – QED correction, proportional to  $H_{\text{D1}}$
- $\delta V_{\text{ret}}$  – accounts for the effect of retardation which switches the behavior of the potential from  $R^{-6}$  to  $R^{-7}$  for very large interatomic distances, short range retardation is identical to the Breit correction

# Comparison of various corrections to the potential



**Higher dispersion coefficients  
for the interaction of helium atoms  
and asymptotics of the adiabatic correction**

## Borna-Oppenheimer energy

- Proper formulas were derived and dispersion coefficients  $C_n$ ,  $n = 11 - 16$ , were calculated.
- This is a first example of systematic and complete calculation of higher than  $C_{10}$  dispersion coefficients for a system different than hydrogen molecule.

## Adiabatic correction

- Formulas for the leading asymptotic coefficients of the adiabatic correction  $A_6$ ,  $A_8$  and  $A_{10}$  were derived.
- This is a first complete and fully correct solution to the problem of the adiabatic correction asymptotics.

# Calculation of the scattering length for metastable helium atoms

# The scattering length for various potentials

Potential	$a$	$\Delta a$
$V$	7.573	
$V + \delta V_{\text{ad}}$	7.352	-0.221
$V + \delta V_{\text{CG}}$	7.761	0.188
$V + \delta V_{\text{ad}} + \delta V_{\text{CG}}$	7.527	-0.046
$V + \delta V_{\text{ret}}$	7.583	0.010
$V + \delta V_{\text{B}}$	7.629	0.056
$V + \delta V_{\text{B}} + \delta V_{\text{ret}}$	7.629	0.056
$V + \delta V_{\text{ad}} + \delta V_{\text{CG}} + \delta V_{\text{B}}$	7.582	0.009
$V + \delta V_{\text{ad}} + \delta V_{\text{CG}} + \delta V_{\text{B}} + \delta V_{\text{QED}}$	7.567	-0.006
all + $\delta V_{\text{ret}}$	7.567	-0.006
Error estimation	0.025	

# Effect of the quality of the Born-Oppenheimer potential on the scattering length

Potential	$a$	$\Delta a$
$V$	7.573	
$V_{\text{CCSD(T)}}$	11.80	4.227
$V_{10}$	10.12	2.547
$V_{12}$	7.594	0.021
$V_{14}$	7.574	0.001

## Caution

Neglecting higher correlation effects overestimates  $a$  by 58%.

Neglecting higher dispersion coefficients overestimates  $a$  by 34%.

# The scattering length for spin-polarized helium. Present state.

Author (year)	$a$ [nm]
Experimental determinations	
Robert <i>et al.</i> (2001)	$20 \pm 10$
Pereira Dos Santos <i>et al.</i> (2001)	$16 \pm 8$
Tol <i>et al.</i> (2004)	$10 \pm 5$
Seidelin <i>et al.</i> (2004)	$11.3^{+2.5}_{-1.0}$
Kim <i>et al.</i> (2005)	$7.2 \pm 0.6$
Moal <i>et al.</i> (2006)	$7.512 \pm 0.005$
Theoretical determinations	
Gadéa <i>et al.</i> (2002)	15.4
Dickinson <i>et al.</i> (2004)	$12.2_{-4.2}$
Tol <i>et al.</i> (2004)	8.3
Przybytek, Jeziorski (2005)	$7.51 \pm 0.20$
Present value	$7.567 \pm 0.025$

- The calculated value of the scattering length is inconsistent with all previous (before 2005) experimental values.
- There is a good agreement between present result  $a = 7.57 \pm 0.03$  nm and the direct measurement of  $a = 7.2 \pm 0.6$  nm, the theoretical value being significantly more accurate.
- There is a disagreement between the newest (2006) experimental-theoretical value  $a = 7.512 \pm 0.005$  nm and theoretical result.
- The calculation can be further improved by including additional effects:
  - nonadiabatic effects
  - spin-dipole interaction

**Thank you for attention**